THERMOPLASTIC AND VISCOELASTIC PROPERTIES OF COALS

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INTRODUCTION

The modern structural view of the organic phase of bituminous and other coals is one of a crosslinked network structure (Larsen and Kovac, 1978; Lucht and Peppas, 1981 a, b; Lucht and Peppas, 1984a; Peppas and Lucht, 1984). In a recent publication (Peppas and Lucht, 1984) we have presented experimental evidence of the crosslinked structure using equilibrium swelling studies and we have offered a model that can be used to analyze it. Dynamic swelling studies using penetrants (Peppas *et al.*, 1983; Lucht and Peppas, 1984b; Peppas *et al.*, 1984; Barr-Howell and Peppas, 1985) have contributed to our understanding of this macromolecular structure.

If coal is a macromolecular network it should be possible to analyze it using theories and experiments widely applicable to polymers, basically theories of viscoelastic and rheological behavior. Since coal is a more complex and inhomogeneous structure, rheological and other analyses can give only an approximate picture of the coal structure, one that will not satisfy the purists, but still one that can offer important new insight.

Of particular importance is any information that can be obtained of the coal structure at temperatures approaching the liquefaction temperatures (300–350°C). It is known (Peppas, 1983) that coal exhibits a glass transition temperature in this range depending on its carbon content and other characteristics. The process of liquefaction is one that involves diffusive, reactive and thermal degradative phenomena; exact molecular information becomes quite difficult to obtain at high temperature. However, by using thermal analysis techniques or a combination of thermal analysis and diffusive techniques it is possible to investigate the relative importance of diffusion and degradation in the overall process. In addition, the associated viscoelastic changes of the coal network, which are expected to occur even significantly below T_g can be quantified by use of simple or sophisticated mechanical experiments (Howell and Peppas, 1984).

It is known that coal at high temperatures, close to the liquefaction temperature of 300–350°C, softens and behaves as a highly viscoelastic material. Its viscosity becomes dependent on the conditions of application of stress or strain. For example, Nazem (1980) studied the non-Newtonian behavior of carbonaceous mesophase pitch at high temperatures using a Haake viscometer and established the non-Newtonian behavior in terms of the viscosity as a function of the shear rate. Briggs investigated the viscosity of coal tar pitch as a function of temperature. Covey and Stanmore (1980) attempted to present a constitutive equation for the rheological behavior of Victorian brown coals of Australia.

An alternative approach of investigation of the viscoelastic behavior of coals is through thermal analysis at high temperatures. The early work of Bangham and Franklin (1946) established characteristics of the change and expansion of the coal structure at high temperatures. Sanada and Honda (1963) used creep deformation of various Japanese coals to establish their mechanical behavior at high temperatures. Gryaznov *et al.* (1977) and Lazarov (1983) examined the thermoplastic behavior of coals and discussed the results of several thermal analysis techniques. They examined the plasticizing phenomena of coals at high temperatures, their anisotropic liquid crystalline formations and their rheological behavior.

Thermogravimetric studies for the purpose of elucidating the thermoplastic behavior has been presented by Rovenskii and Melnik (1975), Ciuryla *et al.* (1979) and Elder and Harris (1984). Probably the most interesting recent studies on this subject are those of the group of Jenkins (Jenkins and Khan, 1982; Khan and Jenkins, 1984 a,b) who used a microdilatometer to investigate changes in the stress-strain behavior of certain coals.

EXPERIMENTAL PART

Coal samples, packed under nitrogen, were supplied by the Pennsylvania State University Coal Bank. They were sieved to the desired mesh size and stored under nitrogen until use.

For the pyridine sorption studies at high temperatures, a thermogravimetric analyzer (Perkin Elmer, model TGA-2, Norwalk, Conn.) and an associated sorption system were used. Approximately 5 mg of the coal sample was placed in a platinum pan which was suspended from a lever arm balance. The system was then emerged in a microfurnace and purged with nitrogen. After one hour pyridine was allowed to bubble through the system and over the coal sample. Changes in weight due to sorption were recorded. The sorption experiments were carried out at constant temperature of 50 °C, 100 °C, 150 °C, 250 °C, 300 °C, and 350 °C.

For the creep experiments a thermomechanical analyzer was used. The flat coal samples for these studies were prepared under nitrogen by slicing coal chunks along their fault lines, and grinding the resulting slabs smooth with a diamond wheel (Peppas *et al.*, 1984). The size of each sample was approximately 2.5 mm^2 in surface area, by 0.6 to 0.9 mm in thickness. The flat samples were cut to the size of the TMA probe and tested using the thermomechanical analyzer (Perkin Elmer, model TMS-2) in the penetration mode under continuous purging with nitrogen. The initial temperature was 35 °C and a scanning rate of 10 °C/min was used. The surface area of the cylindrical probe tip used was 0.6207 mm^2. Each sample was tested using applied loads of 10, 20, 30 and 40 g with corresponding stresses of 0.158, 0.316, 0.474 and 0.632 MPa. Changes due to deformation were recorded.

RESULTS AND DISCUSSION

Dynamic Swelling at High Temperatures

Dynamic swelling experiments with coal particles were performed at various temperatures to establish the transport mechanism in the presence of a solvent and the degradation reaction of coal. The studies presented here were performed with PSOC 312 coal particles of 20-30 mesh at 35, 50, 100, 150, 200, 250 and 300 °C.

The results of these studies are presented in Figures 1 and 2. At low temperatures, 35 and 50 °C, significant pyridine uptake is observed with minimum degradation. At 100 °C degradation is prominent, and the overall change of weight is smaller than at lower temperatures. Above 150 °C the degradation is significant. To further investigate this phenomenon similar coal samples were run in the TGA equipment in the absence of pyridine vapors and the degradation was recorded as shown in Figure 3. Experiments at 35 °C, 50 °C, 100 °C and 150 °C showed no measurable degradation over a period of 15 hours. Then, the data of Figure 1 and 2 were corrected for the loss of weight due to degradation and the corrected values are reported in Figure 4.

The overall penetrant uptake does not, and should not be expected to, correlate with temperature, since, due to the degradation process, the coal structure changes radically, leading to significant changes of the thermodynamic interactions between pyridine and coal network as well as, most probably, the porous structure. However, the inflection points and overshoots observed especially at 200 °C, 250 °C, and 300 °C are "real" observations, since the experimental error of the technique was determined to be less than 0.1 %. The data of 150 °C show that at this temperature the degradation is more significant than the pyridine uptake.

In general we may conclude that the pyridine transport through the significantly altered coal network at temperatures approaching its glass transition temperature is highly non-Fickian, that macromolecular relaxations become extremely important (as exhibited by the strong overshoots observed), and that the affinity of pyridine for the network is dramatically altered at high temperatures. Obviously, more detailed studies are needed to quantitatively elucidate this very fascinating phenomenon.

In the presence of 70-150 % pyridine in coal particles at 250–350 °C the coal network is in the rubbery state, only slightly above its T_g values (Peppas, 1983) and the highly anomalous transport mechanism should be expected, due to the value of the Deborah number which is of the order of one (Peppas *et al.*, 1984). The macromolecular relaxation, and the associated anomalous transport, lead to a drastically increased penetrant flux in the coal network, since the pseudo-convective contribution to anomalous transport becomes extremely important. In fact, no experimental data have been observed before, where at equilibrium the pyridine uptake is as high as 2.3 times the weight of coal, when Fickian diffusion predominates.

Viscoelastic Behavior at Low and High Temperatures

Figures 5 and 6 present the compressive strain versus temperature (and time, since the scanning speed was 10 ° C/min) curves for samples of PSOC-312 with 78.33 % C and PSOC-853 with 80.15 % C, for different applied stresses.

Each curve on Figure 5 shows an induction period, followed by a change of the strain, usually starting at about 115-150 ° C. At about 350 ° C, where the sample is near its glass transition temperature, the compressive strain is only about 3-3.5 % of the total thickness, a typical value of compressive strain for porous, glassy polymers. Almost all the samples show that at low applied stresses and up to 300 ° C a significant "negative strain" (namely expansion) of the coal samples is exhibited, which is, of course, characteristic of the traditional "swelling" of coals when heated in an inert atmosphere. With higher applied stress, the overall effect is compression and therefore an increase in compressive strain.

To further understand the viscoelastic behavior of coal below and near T_g, one may have to further examine Figure 6 which shows the strain versus temperature behavior up to the glass transition region. All the curves are smooth (a minor inflection point of unknown origin appears at about 250 ° C) and quite typical of the similar behavior of glassy polymers. The porous structure should not be of major concern in this analysis. Since coal is glassy in most of the range of temperatures studied here, major pore compression would be unlikely to occur.

At a specific temperature, the creep behavior is highly similar to that of conventional macromolecular structures (Figure 7). A smooth increase in compressive strain is observed, which at 250 ° C (for PSOC-853) seems to level off at about 20 %, whereas at 300 ° C it reaches 65 %. It should be noted that the T_g value for this coal is 305 ° C.

Figure 7 shows also the effect of repeated loadings (or creep experiments) on the compressive strain at constant temperature. For example, at 300 ° C the creep behavior was followed for 200 hours at which time (point A) the load was removed and the recovery process was followed. The sample attained a certain compressive strain of 0.50 (permanent plastic deformation). Upon reapplication of the same stress at 260 hours (point B) a very fast creep behavior was observed. It must be noted that the new values of the compressive strain were on the extrapolated curve of the first creep experiment (see dashed line of Figure 7). A similar behavior is obtained at 250 ° C, although of much smaller magnitude since the coal network is still glassy at this temperature.

One important comment must be made here. In a previous note (Howell and Peppas, 1984) we had discussed our first data with this technique, using coal samples which were bigger than the probe size of the TMA and we had concluded that some coal samples exhibit unusual "plateau" regions during their temperature-dependent creep behavior. In a private communication, Dr. D. Brenner of Exxon pointed out that the phenomenon studied before was that of "squeezing flow" in a viscoelastic matrix. The new studies reported here are with TMA probe-size coal samples (and with much improved preparation techniques which provide samples of truly uniform thickness (Ritger, 1985)), and they truly represented a creep behavior. The plateau region observed in the "squeezing flow" type studies has disappeared here, although a weak inflection point can be seen in some of the samples in the same region where the plateau was before. Obviously, studies towards this direction will continue.

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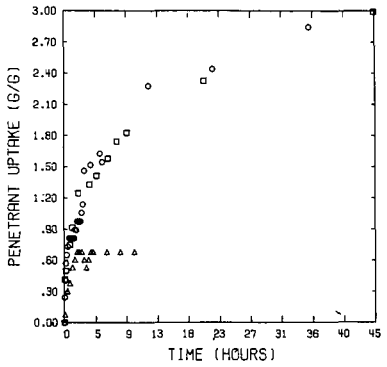

Figure 1: Effect of Swelling Temperature on Pyridine Uptake on Coal Particles of PSOC-312. Temperatures: 35 ° C (○), 50 ° C (□) and 100 ° C (Δ).

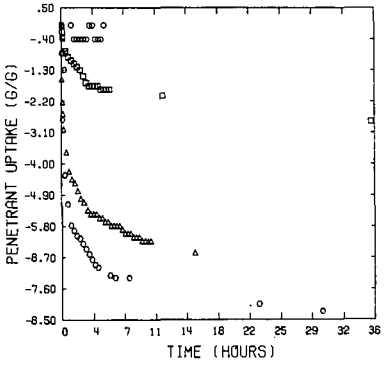

Figure 2: Effect of Swelling Temperature on Pyridine Uptake on Coal Particles of PSOC-312. Temperatures: 150 ° C (○), 200 ° C (□), 250 ° C (Δ), and 300 ° C (◇).

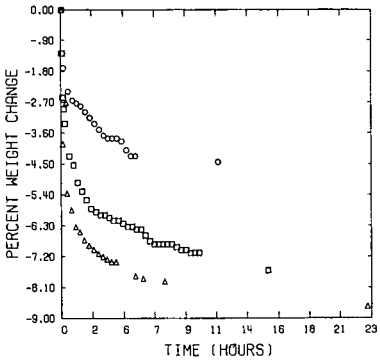

Figure 3: Coal Weight Loss as a Function of Time for PSOC-312. Temperatures: 200 °C (○), 250 °C (□), 300 °C (△).

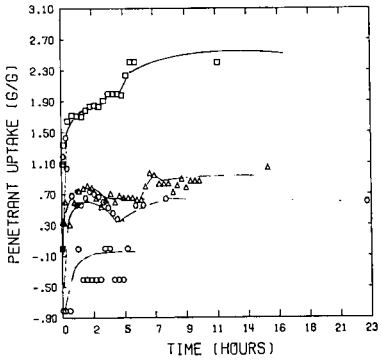

Figure 4: Corrected Pyridine Uptake of PSOC-312. Temperatures: 150 °C (○), 200 °C (□), 250 °C (△), 300 °C (◇).

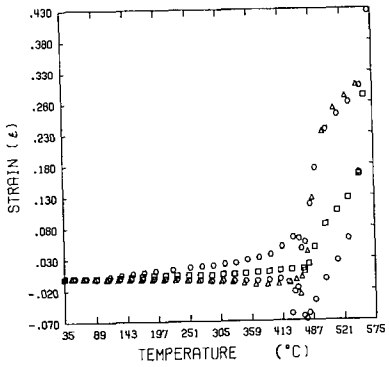

Figure 5: Compressive Strain as a Function of Temperature for Flat Coal Section of PSOC-312 with Applied Stress of 0.158 (○), 0.316 (□), 0.474 (△), and 0.632 (◇) MPa.

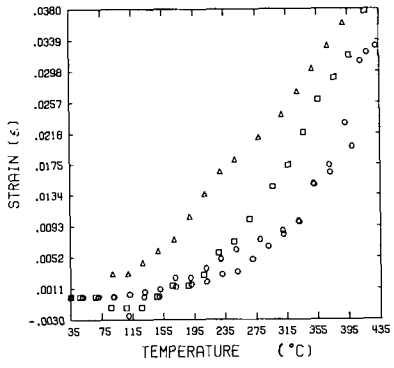

Figure 6: Compressive Strain as a Function of Temperature for Flat Coal Section of PSOC-853 with Applid Stress of 0.158 (○), 0.316 (□), 0.474 (△), and 0.632 (◇) MPa.

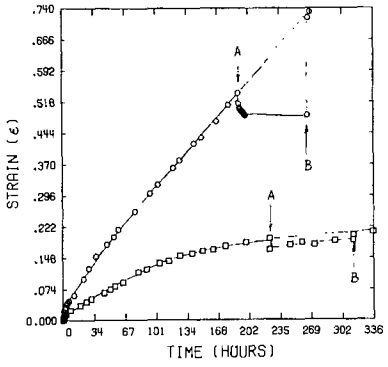

Figure 7: Compressive Strain as a Function of Time for PSOC-853 Coal Samples under Applied Stress of 0.474 MPa at 250 °C (□) and 300 °C (○). Creep period (from 0 to point A); recovery period (from A to B); second creep period (after point B).